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<table style="width: 100%; border: none;"> <tr> <td style="width: 50%; vertical-align: top; padding: 5px;"> <p>(21) International Application Number: PCT/GB94/00461</p> <p>(22) International Filing Date: 9 March 1994 (09.03.94)</p> <p>(30) Priority Data: 9304887.4 10 March 1993 (10.03.93) GB</p> <p>(71) Applicant (for all designated States except US): COUR- TAULDS FIBRES (HOLDINGS) LIMITED [GB/GB]; 50 George Street, London W1A 2BB (GB).</p> <p>(72) Inventor; and (75) Inventor/Applicant (for US only): TAYLOR, James, Martin [GB/GB]; 146 Field Lane, Alvaston, Derby DE2 6GW (GB).</p> <p>(74) Agent: HALE, Stephen, Geoffrey; J.Y. & G.W. Johnson, Furnival House, 14-18 High Holborn, London WC1V 6DE (GB).</p> </td> <td style="width: 50%; vertical-align: top; padding: 5px;"> <p>(81) Designated States: AT, AU, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, ES, FI, GB, GE, HU, JP, KP, KR, KZ, LK, LU, LV, MG, MN, MW, NL, NO, NZ, PL, PT, RO, RU, SD, SE, SI, SK, UA, US, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).</p> <p>Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i></p> </td> </tr> </table>			<p>(21) International Application Number: PCT/GB94/00461</p> <p>(22) International Filing Date: 9 March 1994 (09.03.94)</p> <p>(30) Priority Data: 9304887.4 10 March 1993 (10.03.93) GB</p> <p>(71) Applicant (for all designated States except US): COUR- TAULDS FIBRES (HOLDINGS) LIMITED [GB/GB]; 50 George Street, London W1A 2BB (GB).</p> <p>(72) Inventor; and (75) Inventor/Applicant (for US only): TAYLOR, James, Martin [GB/GB]; 146 Field Lane, Alvaston, Derby DE2 6GW (GB).</p> <p>(74) Agent: HALE, Stephen, Geoffrey; J.Y. & G.W. Johnson, Furnival House, 14-18 High Holborn, London WC1V 6DE (GB).</p>	<p>(81) Designated States: AT, AU, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, ES, FI, GB, GE, HU, JP, KP, KR, KZ, LK, LU, LV, MG, MN, MW, NL, NO, NZ, PL, PT, RO, RU, SD, SE, SI, SK, UA, US, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).</p> <p>Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i></p>
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<p>(54) Title: FIBRE TREATMENT</p> <p>(57) Abstract</p> <p style="margin-top: 20px;">The fibrillation tendency of solvent-spun cellulose fibre is reduced by treating the fibre with a cross-linking agent and a flexible linear polymer with terminal functional groups, for example polyethylene glycol (PEG) of molecular weight 300 to 600. The fibre may be treated in never-dried or in fabric form.</p>				

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- 1 -

FIBRE TREATMENTField of the Invention

This invention is concerned with a method of reducing the fibrillation tendency of solvent-spun cellulose fibre.

Background Art

5 It is known that cellulose fibre can be made by extrusion of a solution of cellulose in a suitable solvent into a coagulating bath. One example of such a process is described in US-A-4,246,221, the contents of which are incorporated herein by way of reference. Cellulose is dissolved in a solvent such as a tertiary amine N-oxide, for
10 example N-methylmorpholine N-oxide. The resulting solution is extruded through a suitable die to produce filaments, which are coagulated, washed in water to remove the solvent and dried. The filaments are generally cut into short lengths at some stage after coagulation to form staple
15 fibre. This process of extrusion and coagulation is referred to as "solvent-spinning", and the cellulose fibre produced thereby is referred to as "solvent-spun" cellulose fibre. It is also known that cellulose fibre can be made by extrusion of a solution of a cellulose derivative into a
20 regenerating and coagulating bath. One example of such a process is the viscose process, in which the cellulose derivative is cellulose xanthate. Both such types of process are examples of wet-spinning processes. Solvent-spinning has a number of advantages over other known
25 processes for the manufacture of cellulose fibre such as the viscose process, for example reduced environmental emissions.

30 Fibre may exhibit a tendency to fibrillate, particularly when subjected to mechanical stress in the wet state. Fibrillation occurs when fibre structure breaks down in the longitudinal direction so that fine fibrils become

- 2 -

partially detached from the fibre, giving a hairy appearance to the fibre and to fabric containing it, for example woven or knitted fabric. Dyed fabric containing fibrillated fibre tends to have a "frosted" appearance, which may be aesthetically undesirable. Such fibrillation is believed to be caused by mechanical abrasion of the fibres during treatment in a wet and swollen state. Wet treatment processes such as dyeing processes inevitably subject fibres to mechanical abrasion. Higher temperatures and longer times of treatment generally tend to produce greater degrees of fibrillation. Solvent-spun cellulose fibre appears to be particularly sensitive to such abrasion and is consequently often found to be more susceptible to fibrillation than other types of cellulose fibre. In particular, cotton has an inherently very low fibrillation tendency.

It has been known for many years to treat cellulose fibre and in particular fabric with a crosslinking agent to improve its crease resistance, as described for example in Kirk-Othmer's Encyclopaedia of Chemical Technology, third edition, Volume 22 (1983), Wiley-Interscience, in an article entitled "Textiles (Finishing)" at pages 769-790, and by H. Petersen in Rev. Prog. Coloration, Vol 17 (1987), pages 7-22. Crosslinking agents may sometimes be referred to by other names, for example crosslinking resins, chemical finishing agents and resin finishing agents. Crosslinking agents are small molecules containing a plurality of functional groups capable of reacting with the hydroxyl groups in cellulose to form crosslinks. One class of crosslinking agents consists of the N-methylol resins, that is to say small molecules containing two or more N-hydroxymethyl or N-alkoxymethyl, in particular N-methoxymethyl, groups. N-methylol resins are generally used in conjunction with acid catalysts chosen to improve crosslinking performance. In a typical process, a solution containing about 5-9% by weight N-methylol resin crosslinking agent and 0.4-3.5% by weight acid catalyst is padded onto dry cellulosic fabric to give 60-100% by weight

- 3 -

wet pickup, after which the wetted fabric is dried and heated to cure and fix the crosslinking agent. In general, more than 50%, often 75%, of the crosslinking agent becomes fixed to the cellulose. It is known that crease-resistant finishing treatments embrittle cellulose fibre and fabric with a consequent loss of abrasion resistance, tensile strength and tear strength. A balance must be struck between improvement in crease resistance and reduction in such other mechanical properties. It is also known that such treatments reduce dyeability.

US-A-4,780,102 describes a process for dyeing a smooth-dry cellulosic fabric which comprises padding the cellulosic fabric with an aqueous finishing solution comprising sufficient concentrations of N-methylol crosslinking agent, acid catalyst and polyethylene glycol (PEG) in order to impart smooth-dry and dye receptivity properties to the fabric; drying and curing the fabric for sufficient time and at sufficient temperature to interact the components of the finish with the fabric; and dyeing the fabric with a cellulose dye. The cellulosic fabric is preferably a cotton fabric. The pad bath typically contains by weight 5-10% crosslinking agent, 0.7-0.8% zinc nitrate hexahydrate and 10-20% PEG. Smooth-dry ratings begin to drop off substantially with PEG molecular weights of 600 or less, and on this basis PEG of molecular weight 600-1450 is preferred depending on the level of smooth-dry performance desired.

Disclosure of the invention

A method according to the present invention for reducing the fibrillation tendency of solvent-spun cellulose fibre is characterised in that it includes the step of contacting the fibre with:

- (a) a flexible linear polymer having terminal functional groups; and
- (b) a crosslinking agent reactive with cellulose and

- 4 -

with said terminal functional groups.

5 The method of the invention may be performed on never-dried fibre or on fabric, for example woven or knitted fabric, containing the fibre. Never-dried fibre is defined as fibre produced in a wet-spinning process, which has been coagulated and washed but which has not been dried.

10 The crosslinking agent may in general be any of those known in the art for crease-resistant finishing of cellulose. The crosslinking agent is preferably an agent classed as a low-formaldehyde or zero-formaldehyde crosslinking agent, further preferably an agent classed as a zero-formaldehyde agent when the method of the invention is carried out on fabric. One class of low-formaldehyde crosslinking agents consists of the N-methylol resins. 15 Examples of suitable N-methylol resins are those described in the abovementioned articles in Kirk-Othmer and by Petersen. Examples of such resins include 1,3-dimethylol-ethyleneurea (DMEU), 1,3-dimethylolpropyleneurea (DMPU) and 4,5-dihydroxy-1,3-dimethylolethyleneurea (DHDMEU). Other 20 examples include compounds based on urones, triazinones and carbamates. Another example of a preferred class of crosslinking agents consists of compounds based on 1,3-dialkyl-4,5-dihydroxy(alkoxy)ethyleneurea, for example 1,3-dimethyl-4,5-dihydroxyethyleneurea. A further example 25 of a suitable crosslinking agent is melamine. Yet another example of a suitable crosslinking agent is butanetetra-carboxylic acid (BTCA).

30 It is known that crosslinking agents for crease-resistant finishing of cellulose are generally used in conjunction with a catalyst, commonly an acid catalyst. The method of the invention preferably utilises such a catalyst when recommended for use with the chosen crosslinking agent. For example, N-methylol resins and 1,3-dialkyl-4,5-dihydroxy(alkoxy)ethyleneureas are 35 preferably used in conjunction with an acid catalyst, for

- 5 -

example an organic acid such as acetic acid or a latent acid such as an ammonium salt, amine salt or metal salt, e.g. zinc nitrate or magnesium chloride. Mixed catalyst systems may be used.

5 The flexible linear polymer is preferably a wholly aliphatic polymer. The backbone of the flexible linear polymer is preferably unbranched. The flexible linear polymer preferably contains no functional groups reactive with cellulose or with the crosslinking agent other than the
10 terminal functional groups. The terminal functional groups are preferably hydroxyl groups, although other types of groups such as amino groups may also be suitable in some cases. Preferred types of flexible linear polymer include polymerised glycols such as polypropylene glycol (PPG) and
15 in particular polyethylene glycol (PEG). Amine-tipped derivatives of such polymerised glycols may be used.

 It will be understood that such flexible linear polymers are generally mixtures of molecules having a range of chain lengths and are characterised in terms of their
20 average molecular weight and chain length. The flexible linear polymer is capable of reacting through its functional groups to provide a linear chain corresponding to the polymer backbone, preferably containing on average about 5 to 150 atoms, more preferably about 10 to 100 atoms, further
25 preferably about 20 to 40 atoms. A preferred example of a flexible linear polymer for use on never-dried fibre is PEG having average molecular weight in the range 100 to 2000, more preferably 200 to 1500, further preferably 300 to 600. In general, use on never-dried fibre of a flexible linear
30 polymer with a backbone shorter than about 5 atoms imparts good fibrillation resistance but an unacceptable reduction in dyeability, whereas use of a flexible linear polymer with a backbone longer than about 150 atoms imparts little reduction in dyeability but only a small improvement in
35 fibrillation resistance. A preferred example of a flexible linear polymer for use on fabric is PEG having average

- 6 -

5 molecular weight in the range 300 to 400. It has been found that fabrics treated with PEG of this molecular weight range exhibit good resistance to fibrillation and good dyeability, whereas fabrics treated with PEG of molecular weight outside this range may possess good resistance to fibrillation but in general exhibit reduced dyeability.

10 The crosslinking agent, flexible linear polymer and any catalyst are preferably contacted with the fibre from solution, preferably an aqueous solution. Polymerised glycols such as PEG and PPG are generally soluble in water.

15 The solution may be applied to never-dried fibre in known types of ways, for example the solution may be padded on to the never-dried fibre or the never-dried fibre may be passed through a treatment bath of the solution. The never-dried fibre may have a moisture content of about 45-55%, often around 50%, by weight, after contacting with the solution. Application of the solution to the never-dried fibre may be carried out in such a way that part or substantially all of the water in the never-dried fibre is replaced by the solution. The never-dried fibre may be in tow or staple form. The solution may contain 0.2 to 15%, preferably 0.5 to 10%, more preferably 0.5 to 5%, by weight crosslinking agent (expressed on a 100% activity basis). The solution preferably contains 0.5 to 5% by weight flexible linear polymer. When a catalyst is used, the solution may contain 0.1 to 5%, preferably 0.25 to 2.5%, by weight catalyst. The solution may contain one or more additional substances, for example a soft finish for the fibre. It is an advantage of the method of the invention as applied to never-dried fibre that it can be combined with another treatment step, such as the application of soft finish.

35 The treated wet never-dried fibre preferably contains 0.2 to 5%, more preferably 0.5 to 2%, by weight crosslinking agent calculated on weight of cellulose. The treated wet never-dried fibre preferably contains 0.5 to 3%

- 7 -

by weight flexible linear polymer calculated on weight of cellulose.

5 The solution may be applied to fabric in known types of ways, for example the solution may be padded onto the fabric or the fabric may be passed through a treatment bath of the solution. The solution may contain 2.5 to 10%, preferably 5 to 7.5%, by weight crosslinking agent (expressed on a 100% activity basis). The solution may contain 5 to 20%, preferably 10 to 15%, by weight flexible linear polymer.
10 When a catalyst is used the solution may contain 0.1 to 5%, preferably 0.25 to 2.5%, by weight catalyst. It has remarkably been observed that in general closely-defined conditions are required for fabric treatment in order to avoid reduction in dyeability of the fabric.

15 It has been observed that treatment of fibre in the never-dried state according to the invention may give rise to roughnesses in spun yarns prepared from the treated fibre, which may be undesirable in some applications. Treatment of fabric according to the invention does not give
20 rise to surface roughnesses.

 In one embodiment of the invention, the crosslinking agent and flexible linear polymer are utilised as separate materials. In another embodiment of the invention, the terminal functional groups in the flexible linear polymer
25 are first reacted with the crosslinking agent to provide a flexible linear polymer having terminal functional groups reactive with cellulose, and never-dried cellulose is subsequently treated with this latter polymer. For example, the crosslinking agent and the flexible linear polymer may
30 react together in solution before application to the fibre.

 After treatment with crosslinking agent and flexible linear polymer according to the invention, the fibre is heated to fix and cure the crosslinking agent and is dried. The heating step may precede, be part of or follow the

- 8 -

drying step. When the method is applied to never-dried fibre, dry staple fibre may be converted to yarn which is then heated to cure and fix the crosslinking agent. The time and temperature required in the heating step depend on the nature of the crosslinking agent and optional catalyst employed. After heating and drying, the fibre may contain about 0.1 to 4%, preferably 0.5 to 2%, by weight fixed crosslinking agent calculated on weight of cellulose. It has generally been found that about 70 to 75% of the crosslinking agent in the wet fibre may become fixed to the cellulose.

Fibre treated according to the method of the invention may subsequently be dyed with conventional dyes for cellulose fibres.

The method of the invention has the advantage that it may be applied to never-dried fibre, so that protection against fibrillation can be provided at an early stage. Never-dried fibre treated according to the invention exhibits little reduction in dyeability compared with untreated fibre. Fibre treated according to the invention has excellent resistance to fibrillation compared with untreated fibre. Fabric made from never-dried fibre treated according to the method of the invention, for example woven or knitted fabric, can be subjected to severe mechanical treatment in the wet state, such as rope dyeing, without excessive fibrillation. The fabric may be laundered with only little or slow loss of the reduction in fibrillation tendency. The method of the invention generally imparts little if any improvement in crease resistance to fabric made from fibre treated in the never-dried state, and it is remarkable that it nevertheless provides effective protection against fibrillation.

Known methods for the manufacture of solvent-spun cellulose fibre include the steps of:

(1) dissolving cellulose in a solvent to form a

- 9 -

- solution, the solvent being miscible with water;
- (ii) extruding the solution through a die to form a fibre precursor;
- 5 (iii) passing the fibre precursor through at least one water bath to remove the solvent and form the fibre; and
- (iv) drying the fibre.

The wet fibre at the end of step (iii) is never-dried fibre and typically has a water imbibition in the range 120-150% by weight. The dried fibre after step (iv) typically has a water imbibition of around 60-80% by weight. Solvent-spun cellulose never-dried fibre is treated according to the method of the invention before it has been dried, that is to say between steps (iii) and (iv).

10

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The invention is illustrated by the following Examples. In each case, the never-dried fibre used was prepared by extruding a solution of cellulose in N-methylmorpholine N-oxide (NMMO) into an aqueous bath and washing the fibre so formed with water until it was essentially free of NMMO.

20

Materials were assessed for degree of fibrillation using the method described below as Test Method 1 and assessed for fibrillation tendency using the techniques described below as Test Methods 2A and 2B.

25 Test Method 1 (Assessment of Fibrillation)

There is no universally accepted standard for assessment of fibrillation, and the following method was used to assess Fibrillation Index (F.I.). Samples of fibre were arranged into a series showing increasing degrees of fibrillation. A standard length of fibre from each sample was then measured and the number of fibrils (fine hairy spurs extending from the main body of the fibre) along the standard length was counted. The length of each fibril was

30

- 10 -

measured, and an arbitrary number, being the product of the number of fibrils multiplied by the average length of each fibril, was determined for each fibre. The fibre exhibiting the highest value of this product was identified as being the most fibrillated fibre and was assigned an arbitrary Fibrillation Index of 10. A wholly unfibrillated fibre was assigned a Fibrillation Index of zero, and the remaining fibres were graded from 0 to 10 based on the microscopically measured arbitrary numbers.

The measured fibres were then used to form a standard graded scale. To determine the Fibrillation Index for any other sample of fibre, five or ten fibres were visually compared under the microscope with the standard graded fibres. The visually determined numbers for each fibre were then averaged to give a Fibrillation Index for the sample under test. It will be appreciated that visual determination and averaging is many times quicker than measurement, and it has been found that skilled fibre technologists are consistent in their rating of fibres.

Fibrillation Index of fabrics can be assessed on fibres drawn from the surface of the fabric. Woven and knitted fabrics having F.I. of more than about 2.0 to 2.5 exhibit an unsightly appearance.

Test Method 2 (Inducement of Fibrillation)

Method 2A (Blender)

0.5 g fibre cut into 5-6 mm lengths and dispersed in 500 ml water at ambient temperature was placed in a household blender (liquidiser) and the blender run for 2 minutes at about 12000 rpm. The fibre was then collected and dried.

- 11 -

Method 2B (Scour, Bleach, Dye)(i) Scour

1 g fibre was placed in a stainless steel cylinder approximately 25 cm long by 4 cm diameter and having a capacity of approximately 250 ml. 50 ml conventional scouring solution containing 2 g/l Detergyl FS955 (an anionic detergent available from ICI plc) (Detergyl is a Trade Mark) and 2 g/l sodium carbonate was added, a screw cap fitted and the capped cylinder tumbled end-over-end at 60 tumbles per minute for 60 minutes at 95°C. The scoured fibre was then rinsed with hot and cold water.

(ii) Bleach

50 ml bleaching solution containing 15 ml/l 35% hydrogen peroxide, 1 g/l sodium hydroxide, 2 g/l Prestogen PC (a bleach stabiliser available from BASF AG) (Prestogen is a Trade Mark) and 0.5 ml/l Irgalon PA (a sequestrant available from Ciba-Geigy AG) (Irgalon is a Trade Mark) was added to the fibre and a screw cap fitted to the cylinder. The cylinder was then tumbled as before for 90 minutes at 95°C. The bleached fibre was then rinsed with hot and cold water.

(iii) Dye

50 ml dyeing solution containing 8% on weight of fibre Procion Navy HER 150 (a reactive dye) (Procion is a Trade Mark of ICI plc) and 55 g/l Glauber's salt was added and the cylinder was capped and tumbled as before for 10 minutes at 40°C. The temperature was raised to 80°C and sufficient sodium carbonate added to give a concentration of 20 g/l. The cylinder was then capped once more and tumbled for 60 minutes. The fibre was rinsed with water. 50 ml solution containing 2 ml/l Sandopur SR (a detergent available from Sandoz AG) (Sandopur is a Trade Mark) was then added and the

- 12 -

cylinder capped. The cylinder was then tumbled as before for 20 minutes at 100°C. The dyed fibre was then rinsed and dried.

Method 2A provides more severe fibrillating conditions than
5 Method 2B.

Example 1

Never-dried solvent-spun cellulose fibre was immersed in a bath containing varying levels of 1,3-dimethyl-4,5-dihydroxyethyleneurea (available from
10 Hoechst AG under the Trade Mark Arkofix NZF), Catalyst NKD (a magnesium chloride/acetic acid catalyst available from Hoechst AG) (25% by weight on Arkofix NZF), polyethylene glycol (PEG) of various average molecular weights (MW), and
15 DP3408 (a polyether/polyacrylic system available from Precision Processes (Textiles) of Ambergate, Derbyshire). The fibre was then dried at a temperature of 100°C followed by curing at 170°C for 20 seconds. The fibre was then assessed for fibrillation tendency by Test Method 2A. Fibrillation Index (F.I.) results are shown below in Table
20 1A:

Table 1A

	Trial	Arkofix NZF g/l	DP3408 g/l	PEG g/l	PEG MW (top row) and FI (body of table)					
					200	300	400	600	1500	2000
25	1	30	5	10	1.8	0.2	0.1	0.6	3.0	2.8
	2	30	10	20	2.0	1.5	0.1	1.3	1.1	2.4
	3	30	20	30	3.1	1.1	0.8	0.3	2.6	2.4
	4	50	5	20	0.7	2.1	1.7	1.7	0.4	3.2
	5	50	10	30	0.3	1.3	1.3	1.9	1.9	2.5
30	6	50	20	10	1.9	1.3	0.5	1.7	3.3	2.0
	7	80	5	30	1.7	0.1	0.1	1.1	0.8	0.5
	8	80	10	10	0.1	1.4	0.6	2.1	0.3	1.7
	9	80	20	20	1.4	0.6	0.1	0.7	1.2	2.4
	Average				1.4	1.1	0.6	1.3	1.6	2.2

A control sample of untreated fibre exhibited a Fibrillation Index of 5.0.

Experiments which gave good values of Fibrillation

- 13 -

Index at each molecular weight of PEG were repeated, and the results are shown below in Table 1B:

Table 1B

	Arkofix NZF g/l	DP3408 g/l	PEG g/l	PEG MW	F.I.
5	50	10	10	200	0.2
	80	10	30	300	0.0
	80	10	30	400	0.0
10	80	20	10	600	0.2
	80	10	20	1500	3.0
	80	5	30	2000	1.8

Example 2

Never-dried solvent-spun cellulose fibre was immersed in baths containing varying levels of Arkofix NZF, Catalyst NKD (25% by weight on Arkofix NZF) and PEG of average molecular weight 300. The fibre was then dried at 100°C and cured for 20 seconds at 170°C. Fibrillation was induced using Test Method 2A, or 2B, or 2B followed by 2A, and F.I. was assessed using Test Method 1. Results are shown below in Table 2:

Table 2

	Arkofix NZF g/l	PEG 300 g/l	2A	Fibrillation Index 2B	2B+2A
25	50	10	0.0	0.9	3.3
	30	10	0.0	1.9	3.8
	70	30	0.6	0.4	1.6
	Control	-	5.2	-	-

Example 3

Never-dried solvent-spun cellulose fibre was immersed in a bath containing varying levels of Arkofix NZF, magnesium chloride catalyst (25% by weight on Arkofix NZF) and PEG of average molecular weight 400 (30 g/l). The fibre was then dried at 100°C and cured for 20 seconds at 170°C. Fibrillation was induced using Test Method 2A, or 2B followed by 2A, and F.I. was assessed using Test Method 1. F.I., tenacity and extensibility results are shown below in Table 3:

- 14 -

Table 3

	Arkofix NZF g/l	Fibrillation Index 2A	Fibrillation Index 2B+2A	Tenacity cN/tex	Extensibility %
5	30	0.0	1.8	40.1	12.4
	50	1.2	1.6	38.8	11.7
	70	0.0	1.4	39.9	10.4
	90	0.0	5.4	40.6	11.1
	110	0.0	7.2	40.1	9.9
	Control	5.2	-	41.2	12.2

10

Example 4

Never-dried solvent-spun cellulose fibre was immersed in baths containing varying levels of Arkofix NZF, Catalyst NKD (25% by weight on Arkofix NZF) and PEG of average molecular weight 300. The fibre was then dried at 100°C and
 15 cured for 20 seconds at 170°C. The fibre was then dyed under standard conditions and its dyeability expressed in terms of its dye uptake as a percentage of the dye uptake of an untreated control sample. The results shown in Table 4 were obtained:

20

Table 4

	Arkofix NZF g/l	PEG 300 g/l	Dyeability %
25	0	0	100
	70	10	91.9
	90	30	90.4
	70	0	60

It will be observed that dyeability was very markedly reduced in the comparative experiment in which PEG was omitted.

Example 5

30 Woven fabric of solvent-spun cellulose fibre was padded with solutions containing varying amounts of Arkofix NZF, varying amounts of PEG of varying molecular weights, and magnesium chloride as catalyst (25% by weight on Arkofix NZF). The fabrics were dried at 110°C and then heated at
 35 160°C for 30 seconds to cure the resin. The fabrics were dyed with an HE-type reactive dye, and fibrillation was

- 15 -

assessed before and after laundering at 60°C (10 wash/tumble cycles). The results shown in Table 5 were obtained:

Table 5

5	Arkofix NZF g/l	M.W.	PEG g/l	Dyeability %	F.I.	
					Unlaundered	Laundered
	0	-	0	100	1.8	6.4
	70	200	50	83.4	0.2	2.0
	70	200	100	88.0	0.0	1.8
	100	200	50	54.8	0.0	1.0
10	100	200	100	85.3	0.0	1.6
	130	200	50	92.8	0.0	1.4
	130	200	100	100.1	0.0	2.0
	70	300	50	68.4	0.6	2.4
	70	300	100	71.5	0.0	3.8
15	100	300	50	68.0	0.0	2.0
	100	300	100	97.1	0.2	1.6
	130	300	50	65.0	0.0	0.8
	130	300	100	75.7	0.2	1.0
	70	400	50	85.8	0.0	2.4
20	70	400	100	100.7	0.0	3.6
	100	400	50	69.3	0.0	0.8
	100	400	100	85.9	0.0	0.8
	130	400	50	67.4	0.0	0.4
	130	400	100	92.3	0.0	0.4
25	70	600	50	40.3	0.0	3.2
	70	600	100	42.8	0.2	3.6
	100	600	50	51.3	0.0	1.2
	100	600	100	72.7	0.0	1.6
	130	600	50	44.0	0.0	0.6
30	130	600	100	57.6	0.0	0.4

Use of low-formaldehyde resins adversely affected dyeability in comparison with the zero-formaldehyde resin used in the above experiments.

Example 6

35 Never-dried solvent-spun cellulose fibre was treated with an aqueous solution containing Arkofix NZF (40 g/l), PEG 400 (24 g/l) and magnesium chloride (10 g/l) and dried. The treated fibre was spun into yarn, which was knitted into a fabric. The fabric was heated at 150°C for 1 minute to
 40 cure the resin, dyed and assessed for fibrillation after laundering, with the results shown in Table 6A:

- 16 -

Table 6A

	Laundrying cycles	F.I.
5	0	2.0
	3	1.5
	5	2.5
	8	3.8

The fabric appeared hairy, as did the yarn from which it was made. Fabric hand was very soft even without the use of any softening treatment.

Scoured knitted fabric of solvent-spun cellulose was padded with an aqueous solution containing the zero-formaldehyde resin Quecodur FF (Trade Mark of Thor Chemicals) (160 g/l), PEG 400 (100 g/l) and magnesium chloride (40 g/l). The treated fabric was dried and heated at 150°C for 1 minute to cure the resin. The fabric was satisfactorily dyed to medium-dark shade with reactive dyes and assessed for fibrillation after laundering, with the results shown in Table 6B:

20

Table 6B

	Laundrying cycles	F.I.
25	0	0.4
	3	0.8
	5	1.3
	8	1.1

The fabric appeared extremely clean both before and after laundering.

- 17 -

CLAIMS

1. A method for reducing the fibrillation tendency of solvent-spun cellulose fibre, characterised in that it includes the step of contacting the fibre with:

5 (a) a flexible linear polymer having terminal functional groups; and

(b) a crosslinking agent reactive with cellulose and with said terminal functional groups.

2. A method according to claim 1, characterised in
10 that the fibre is contacted with an aqueous solution of the flexible linear polymer and the crosslinking agent.

3. A method according to claim 1 or claim 2, characterised in that the crosslinking agent is a low-formaldehyde or zero-formaldehyde crosslinking agent.

15 4. A method according to claim 3, characterised in that the fibre is additionally contacted with an acid catalyst for the crosslinking agent.

5. A method according to any one of the preceding claims, characterised in that the flexible linear polymer is
20 a wholly aliphatic polymer.

6. A method according to claim 5, characterised in that the flexible linear polymer is polyethylene glycol.

7. A method according to any one of the preceding claims, characterised in that it includes the step of
25 subsequently heating the fibre to fix and cure the crosslinking agent.

8. A method according to any one of the preceding claims, characterised in that the fibre is subsequently

- 18 -

dyed.

9. A method according to any one of the preceding claims, characterised in that the fibre is never-dried solvent-spun cellulose fibre.

5 10. A method according to claim 9, characterised in that the flexible linear polymer is polyethylene glycol of average molecular weight in the range 300 to 600.

11. A method according to claim 9 or claim 10, characterised in that the fibre is contacted with an aqueous
10 solution containing 0.5 to 5 per cent by weight of the crosslinking agent (expressed on a 100% activity basis).

12. A method according to any one of claims 9 to 11, characterised in that the fibre is contacted with an aqueous solution containing 0.5 to 5 per cent by weight of the
15 flexible linear polymer.

13. A method according to any one of claims 1 to 8, characterised in that the fibre is present in a woven or knitted fabric.

14. A method according to claim 13, characterised in
20 that the flexible linear polymer is polyethylene glycol of average molecular weight in the range 300 to 400.

15. A method according to claim 14, characterised in that the fabric is contacted with an aqueous solution containing 10 to 15 per cent by weight of the polyethylene
25 glycol.

16. A method according to any one of claims 13 to 15, characterised in that the crosslinking agent is a zero-formaldehyde resin.

17. A method according to any one of claims 13 to 16,

- 19 -

characterised in that the fabric is contacted with an aqueous solution containing 5 to 7.5 per cent by weight crosslinking agent (expressed on a 100% activity basis).

18. Solvent-spun cellulose fibre with a reduced tendency to fibrillation, characterised in that it has been treated according to the method of any one of the preceding claims.

INTERNATIONAL SEARCH REPORT

Inter. Natl Application No
PCT/GB 94/00461

A. CLASSIFICATION OF SUBJECT MATTER

IPC 5 D01F11/02 D01F2/00 D06M15/53 D06M15/423 D06M13/425
D06M13/432

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 5 D01F D06M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US,A,4 971 708 (SUNG-IN LEE) 20 November 1990 see column 2, line 50 - column 3, line 53; claims	1-8, 13-17
Y	---	9-12, 18
Y	WO,A,92 07124 (COURTAULDS PLC.) 30 April 1992 see the whole document	9-12, 18
P,A	---	
	EP,A,0 538 977 (COURTAULDS PLC.) 28 April 1993 see the whole document	1-18
A	---	
	US,A,3 960 983 (WERNER JOSEF BLANK) 1 June 1976 see abstract; claims	1

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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

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Date of mailing of the international search report

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INTERNATIONAL SEARCH REPORT

Inter. Appl. Application No
PCT/GB 94/00461

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>JOURNAL OF THE TEXTILE INSTITUTE vol. 78, no. 5 , 1987 , MANCHESTER GB pages 357 - 361 P.PAVLOV AND E. LOZANOV 'Properties of Viscose Fibres Modified in an As-spun State by Cross-linking' see abstract -----</p>	1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/GB 94/00461

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A-4971708	20-11-90	NONE	
WO-A-9207124	30-04-92	EP-A- 0552270 JP-T- 6501994	28-07-93 03-03-94
EP-A-0538977	28-04-93	JP-A- 5117970 US-A- 5310424	14-05-93 10-05-94
US-A-3960983	01-06-76	BE-A- 835586 CA-A- 1068036 DE-A- 2551276 FR-A- 2332304 GB-A- 1523466 NL-A- 7513728 US-A- 3959202	14-05-76 11-12-79 26-05-77 17-06-77 31-08-78 27-05-77 25-05-76

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